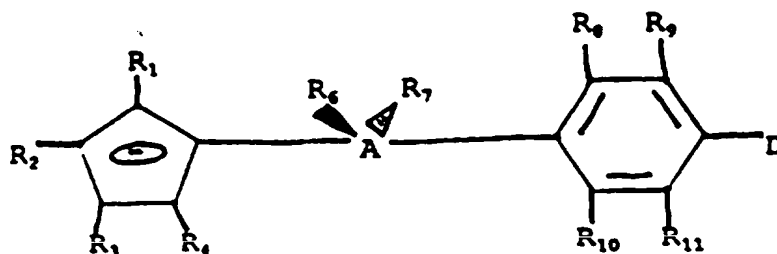




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<b>(21) International Application Number:</b> PCT/US97/11074 <b>(22) International Filing Date:</b> 25 June 1997 (25.06.97)  <b>(30) Priority Data:</b> 08/677,800 10 July 1996 (10.07.96) US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).  <b>(72) Inventors:</b> BONCELLA, James, M.; 2016 N.W. 35th Street, Gainesville, FL 32605 (US). RICHARDSON, David, E.; 3618 N.W. 40th Street, Gainesville, FL 32606 (US). SHAFIQ, Faisal, A.; Apartment 17, 3600 S.W. 19th Avenue, Gainesville, FL 32607 (US).  <b>(74) Agents:</b> SCHNELLER, Marina, V. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		<b>(81) Designated States:</b> AU, CA, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** BRIDGED METALLOCENE COMPOUNDS**(57) Abstract**

The invention relates to new transition metal compounds useful as olefin polymerization catalysts. They are characterized by the formula (V) (E) (W)M(L), in which M is a transition metal, V, E, and W, is e.g. alkyl, and L is a ligand which has formula (I).

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- 1 -

## BRIDGED METALLOCENE COMPOUNDS

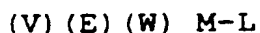
The invention relates to new metallocene compounds. In particular, the new compounds are metallocenes of the transition metals selected from the group consisting of hafnium, titanium and zirconium. These compounds can be used as the source of the transition metal in an olefin polymerization catalyst.

The compounds of the invention comprise those of formula (V) (E) (W) M-L. Preferred compounds within that formula are compounds of formula IA and IB which are defined below;



The element L is a ligand defined below, M is a metal selected from the group consisting of zirconium, hafnium and titanium, X is the same or different and is halide (chloride, bromide or iodide) or alkyl, preferably methyl, or aryl; and Y is preferably alkyl. The group Cp' is an unsubstituted or substituted cyclopentadienyl group. Compounds of formula IA can be used in combination with alumoxane to polymerize ethylene. Compounds of IB can be used in the zwitterionic form to polymerize ethylene, without an alumoxane component for activation of the transition metal.

The invention relates to transition metal compounds, to their synthesis, and to their use in olefin polymerization, which can be characterized by the formula I', where I' is



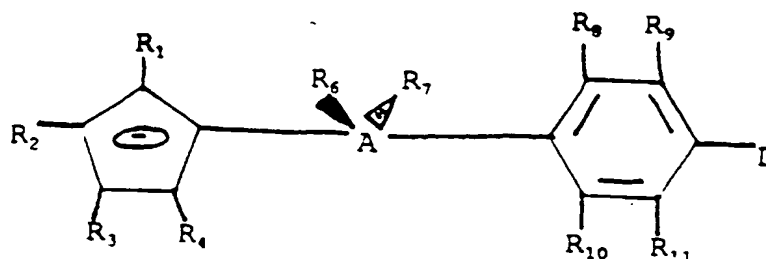
in which M is selected from the group consisting of zirconium, hafnium and titanium;

each of V, E and W is the same or different and is independently alkyl of 1 to 6 carbon atoms, halide, or unsubstituted or substituted cyclopentadienyl,

provided that one, and only one, of said V, E, and W is unsubstituted or substituted cyclopentadienyl; and

- 2 -

in which L is



wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

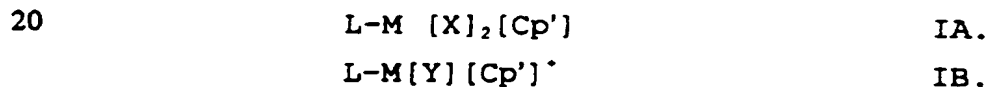
5     A is C, Si, Ge; and each of  $R_6$  and  $R_7$  is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

10     each of  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

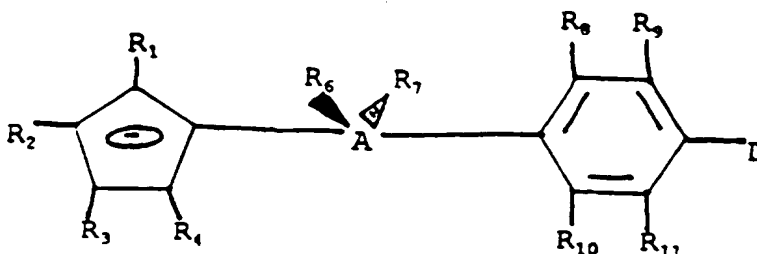
15     D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; and  $BG_3$  or  $AlG_3$ , in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

Preferred compounds of I' are the compounds of formula IA and IB,



L refers to a ligand which has the formula



in which each of 1, 2, 3 and 4 is hydrogen, alkyl of 1 to 6 carbon atoms [including methyl, ethyl, propyl, butyl, isobutyl pentyl isomers of pentyl and hexyl and isomers of hexyl], alkylene of 2 to 10 carbon atoms which form bridged  
5 bicyclic or tricyclic moieties, (such as indenyl);

A is C, Si, Ge,; and each of  $R_6$  and  $R_7$  is the same or different and is alkyl of 1 to 20, preferably 1 to 6, carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

10 each of  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , is the same or different, and is fluorine, hydrogen, or alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal (e.g. sodium or lithium), halogen (chloride or bromide); alkyl halide in which the alkyl has 1 to 6 carbon  
15 atoms and halide is chlorine or bromine, and  $BG$ , or  $AlG$ , in which B is boron (B) or aluminum (Al),

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms, and M is defined as above.

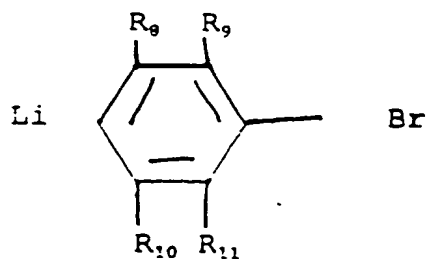
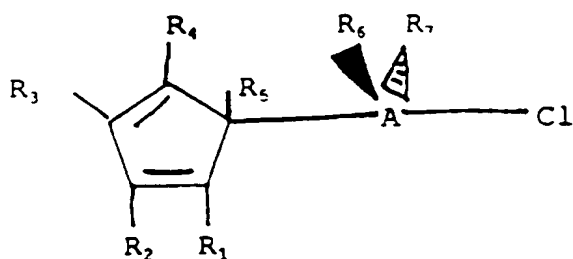
20 In the formula, the  $Cp'$  group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be straight-or branched chain  $C_1$ - $C_6$  alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such  
25 as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. The cyclopentadienyl groups and L can be also substituted or bridged by polymethylene or dialkylsilane groups, such as -  
30  $CH_2$ -,  $-CH_2-CH_2$ -,  $-CR'R''$ - and  $-CR'R''-CR'R''$ - where  $R'$  and  $R''$  are short alkyl groups or hydrogen,  $-Si(CH_3)_2$ -,  $Si(CH_3)_2-CH_2-CH_2$ -  $Si(CH_3)_2$ - and similar bridge groups. Suitable groups constituting  $Cp'$  include unsubstituted or substituted cyclopentadienyl. Substituted cyclopentadienyls include  
35 mono-, di- tri-, tetra- and penta-substituted

cyclopentadienyls in which the substituents are alkyl of 1 to 6 carbon atoms (including methyl, ethyl, propyl, butyl, isobutyl, pentyl, isomers of pentyl, hexyl and isomers of hexyl or alkylene groups of 3 to 10 carbon atoms which form bicyclic and tricyclic alicyclic groups. The cyclopentadienyl ring may be mono-, di-, tri-, tetra or penta-substituted. The substitution may be alkyl of 1 to 6 carbon atoms; and thus includes the methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, methylethylcyclopentadienyl, propylcyclopentadienyl, methylpropylcyclopentadienyl, butylcyclopentadienyl, methylbutylcyclopentadienyl, and hexylcyclopentadienyl, and an indenyl group, 4,5,6,7-tetrahydroindenyl group and fluorenyl group. These cyclopentadienyl groups may be substituted by a halogen atom or trialkylsilyl group. The lithium compound may comprise said cyclopentadienyl substituted by a second cyclopentadienyl bonded together via an alkylene group such as ethylene and propylene, an isopropylidene group, a substituted alkylene group such as diphenylmethylene, a silylene group or a substituted silylene group such as dimethylsilylene, diphenylsilylene and methylphenylsilylene. The di-, tri-, tetra or penta-substituted cyclopentadienyl groups can be dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and isomers of butyl, pentyl, hexyl.

The ligand L can be synthesized from compounds of formula 1.

The initial synthesis step comprises contacting the compound of formula 1 with a compound of formula a,

- 5 -

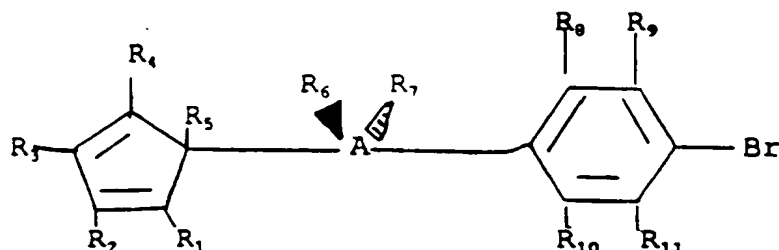


(1)

(a)

in these compounds of formulae 1 and a, each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ , and  $R_{11}$ , and A are as defined above; and  $R_5$  is preferably hydrogen, although it may be  $\text{GeZ}$ , wherein Ge is germanium and Z is alkyl of 1 to 6 carbon atoms [including methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl and isomers of pentyl and hexyl and isomers of hexyl] or aryl of 6 to 10 carbon atoms. In preferred embodiments,  $R_5$  is hydrogen while each of  $R_1$ - $R_4$  is methyl; the kinetic inertness of the tetramethylcyclopentadiene proton, when  $R_5$  is hydrogen, allows preferential nucleophilic displacement of the A-Cl bond in compound 1 as well as lithiation of component 2 resulting in the high yield synthesis of the compound of formula 4, in subsequent steps. Contact of the two compounds can be undertaken at low temperatures, preferably below ambient temperatures in diethyl ether, for extended periods of time. Compounds of formula I in which  $R_1$ - $R_4$ ,  $R_6$  and  $R_7$  are methyl and A is Si (silicon) are readily available. In preferred embodiments herein the compound of formula a is 1,lithium-4,bromo,-2,3,5,6-tetrafluorophenyl.

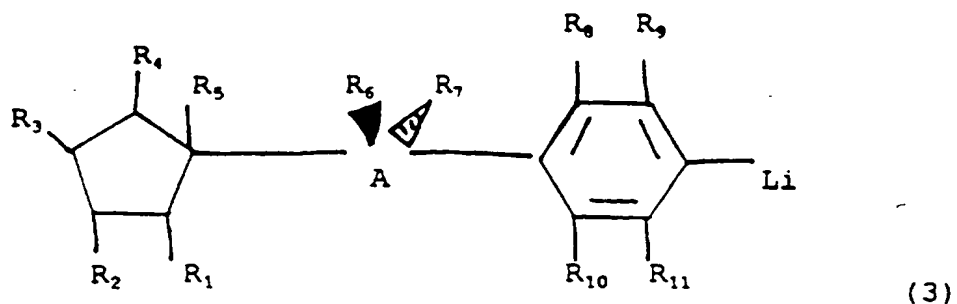
A compound of formula 2 is the product of the contact of the compound of formula 1 and formula a, which is isolatable as a solid compound. The formula of compound(s) 2 is



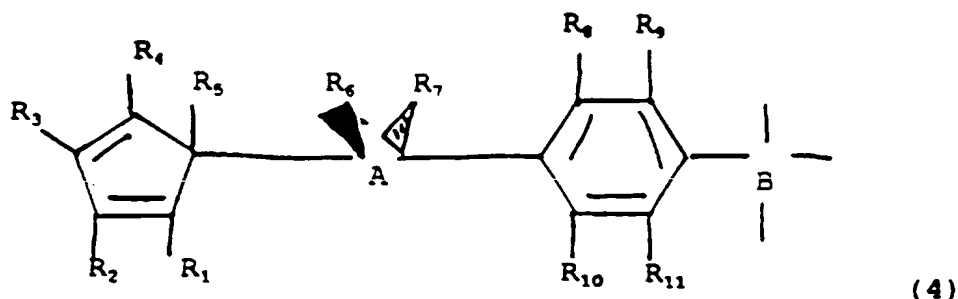
(2)

- 6 -

When D is bromine in compound 2, that compound can be further treated with either an alkyl lithium [n-butyllithium] or a Grignard reagent, and subsequently with  $B(C_6F_5)_3$  to produce a compound 4, wherein D is  $-[B(C_6F_5)_3]$  anion. The sequence can be illustrated by the reactions to yield compounds of formulae 3 and 4. Reaction of compound 2 with BuLi will produce a compound of formula 3, which has the structure



This reaction is undertaken at temperatures below ambient temperature, preferably at  $-78^\circ\text{C}$ , in diethyl ether. Without isolation, the compound of formula 3 is contacted under substantially the same conditions with  $B(C_6F_5)_3$ , at  $-78^\circ\text{C}$ , in diethyl ether for twelve hours to produce the compound of formula 4.



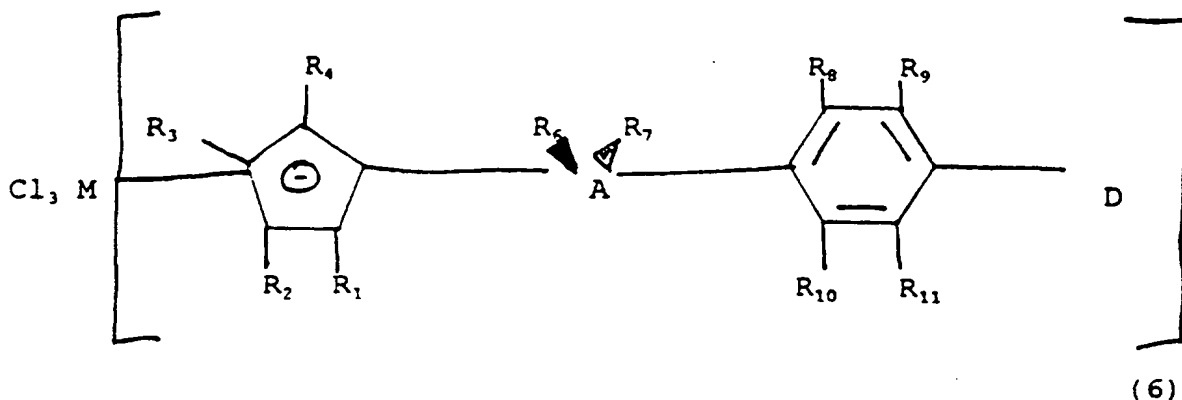
The compound of formula 4 can be converted to a dianion form by abstracting  $R_3$  by treatment with alkyl lithium compounds; this step is conducted in diisopropyl ether, which is essential to facilitate the isolation and purification of the compound 4 when it is a dianion, as for example when D is  $-BG_3$  in formula 5 and G is  $C_6F_5$ .

After formation of the of the compound 5, it is contacted with a transition metal chloride, in which the



- 7 -

transition metal M is titanium, zirconium or hafnium (III or IV), for example, the tetrahalide or tetrachloride of zirconium, hafnium or titanium. The reaction results in production of a transition metal compound of formula 6



Reaction of the compound of formula 6 with a lithium cyclopentadienyl derivative [in which cyclopentadienyl is denoted by Cp'], in methylene chloride at below ambient temperatures [at -78°C] results in production of transition metal compound containing two cyclopentadienyl groups which is the compound of formula IA, above.

The cyclopentadienyl moiety in the lithium compound used to convert compound of formula 6, to the compound of formula 1A can be unsubstituted or substituted; if substituted, the cyclopentadienyl ring may be mono-, di-, tri-, tetra or penta-substituted. The substitution may be alkyl; and thus includes the methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, methylethylcyclopentadienyl, propylcyclopentadienyl, methylpropylcyclopentadienyl, butylcyclopentadienyl, methylbutylcyclopentadienyl, and hexylcyclopentadienyl, and an indenyl group, 4,5,6,7-tetrahydroindenyl group and fluorenyl group. These cyclopentadienyl groups may be substituted by a halogen atom or trialkylsilyl group. The lithium compound may comprise said cyclopentadienyl substituted by a second cyclopentadienyl bonded together via

an alkylene group such as ethylene and propylene, an isopropylidene group, a substituted alkylene group such as diphenylmethylenes, a silylene group or a substituted silylene group such as dimethylsilylene, diphenylsilylene and methylphenylsilylene. The di-, tri, tetra or penta-substituted cyclopentadienyl groups can be dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, and isomers of butyl, pentyl, hexyl. Lithium cyclopentadienyl derivatives are readily commercially available.

Reaction of compound of formula IA with a Grignard reagent or an alkyl lithium reagent results in displacement of the halides by alkyl groups to produce compounds of formula IA in which X is alkyl, provided by the Grignard.

Compounds of formula IA can be converted to compounds of formula IB by contacting the alkylated (wherein X is alkyl of 1 to 6 carbon atoms) IA materials with a borane compound including but not limited to  $B(C_6F_5)_3$ ,  $Ph_3C^+B(C_6F_5)_4^-$  or  $HNR_2Ph^+B(C_6F_5)_4^-$  to abstract an alkyl X group and convert the transition metal compound to a zwitterion for use in polymerization without alumoxane activation. The zwitterion compounds of formula IB may be exemplified by the expression  $(V)(E)(L)M^+$  or  $(V)(W)(L)M^+$  or  $(E)(W)(L)M^+$ , in which L includes the group D which is  $BG_3$  or  $AlG_3$  in which B is boron (B) or aluminum (Al), sodium lithium or halogen and G is selected from the group consisting of pentafluorophenyl, bistrifluoromethylphenyl, hydrogen and alkyl of 1 to 6 carbon atoms. In a catalyst composition the transition metal compounds of IA can be combined with an alumoxane, to activate the compound IA; the amount of alumoxane provides an  $Al[alumoxane]: transition\ metal$  ratio of 50 to 10,000.

Aluminoxanes, e.g. methylalumoxane (MAO), have been used as co-catalyst with metallocene catalysts. The class of alumoxanes (used interchangeably hereinafter with

"aluminoxane") comprises oligomeric linear and/or cyclic alkylaluminumoxanes represented by the formula:  $R-(Al(R)-O)_n-AlR_2$  for oligomeric, linear aluminoxanes and  $(-Al(R)-O)_m$  for oligomeric cyclic aluminoxane wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C1-C8 alkyl group and preferably methyl.

Methylaluminumoxane is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts, such as  $CuSO_4 \cdot 5H_2O$  or  $Al_2(SO_4)_3 \cdot 5H_2O$ . Methylaluminumoxane can be also generated in situ in polymerization reactors by adding trimethylaluminum and water or water-containing inorganic salts. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. MAO is typically kept in solution in toluene.

Conditions for the polymerization and copolymerization of ethylene

The process of the invention may be undertaken in gas phase, in fluid bed gas phase, or in slurry. The catalyst of the invention, allows for the production of linear low density polyethylene in the gas phase or in a slurry polymerization. The products from both the gas phase (e.g. fluid bed) and slurry have a high bulk density, which allows for increased throughput of product per weight of catalyst.

Preferably, the polymerization (copolymerization) is undertaken at a temperature and/or pressure below the sintering temperature of the polymer particles. Most preferably, the process is undertaken in the fluid bed gas phase or in a slurry reactor. The high activity of the catalysts herein allow for efficacious low pressure fluid bed gas phase and/or slurry process product production. Much lower activity catalysts than those described herein are employed in high pressure processes at pressures which exceed 400 psi, such as solution and high pressure slurry polymerizations. For the production of ethylene copolymers in the

process of the present invention an operating temperature of 30° to 115°C is preferred, and a temperature of 70° to 106°C is most preferred. Temperatures of 75° to 90°C are used to prepare products having a density of 0.91 to 0.92, and  
5 temperatures of 80° to 100°C are used to prepare products having a density of 0.92 to 0.94, and temperatures of 90° to 115°C are used to prepare products having a density of 0.94 to 0.96.

In the gas phase, linear low density production is  
10 conducted at 85°C and high density product is formed at 105°C. In slurry polymerization, linear low density production is conducted at 70°C and high density production is conducted at 90°C.

In polymerizations described herein, pressures are below  
15 10000 psi, preferably below 1000 psi. The fluid bed reactor is operated at pressures of up to 1000 psi, and is preferably operated at a pressure of from 150 to 350 psi, with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat  
20 capacity of the gas.

#### Examples

Preparation of  $(C_5(CH_3)_4H-Si(CH_3)_2-p-C_6F_4Br)$  (1): n-BuLi (16.8 mL, 1.6M in hexanes) was carefully injected over a 5 minute period to a -78°C  $Et_2O$  (100 mL) suspension of 1,4-  
25 dibromo 2,3,5,6 tetrafluorobenzene ( $C_6Br_2F_4$ ) (12.9 g) and stirred for 10 min. (Caution: n-BuLi addition must be slow and the solution must be kept cold to prevent formation of benzyne and LiF). A  $Et_2O$  (15 mL) solution of chlorodimethylsilyl tetramethyl cyclopentadiene  $(CH_3)_4(C_5)Si(CH_3)_2-$   
30  $Cl)H$  (8.97 g) was then cannulated over a 7-8 minute period into the flask containing  $LiC_6F_4Br$ . A yellow solution formed immediately. The solution was left stirring at -78°C for 1 hour and then warmed to -50°C for an additional -10 hours.

- 11 -

After this time, the reaction was allowed to warm to room temperature overnight. Stirring was then stopped, to let the salts settle over a one hour period. The remaining yellow solution was separated by cannula filtration. Removal of solvent from the filtrate left an orange oily solid.  
5 Recrystallization from pentane at  $-78^{\circ}\text{C}$  left a pale yellow oily solid. Yield 15.0 g, 88%.

Preparation of  $(\text{C}_5(\text{CH}_3)_4\text{H}-\text{Si}(\text{CH}_3)_2-\text{p}-\text{C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{Et}_2\text{O})_4)$  (2): n-BuLi (1.56 mL, 2.5 M in hexanes) was slowly syringed into a  $-78^{\circ}\text{C}$   $\text{Et}_2\text{O}$  (~20 mL) solution of 1 (1.6 g) and stirred for 10 min. This mixture was then quickly added via cannula to a  $-78^{\circ}\text{C}$   $\text{Et}_2\text{O}$  (~40 mL) solution of  $\text{B}(\text{C}_6\text{F}_5)_3$ . Immediately upon addition a yellow solution formed. The flask was stirred at  $-78^{\circ}\text{C}$  for an additional 14 hours and then left to warm to room temperature overnight. The product formed a yellow solution. Solvent was removed under vacuum and the product was washed 2x with ~20 mL pentane. After pumping dry, a white crystalline solid was isolated. Yield 3.2 g, 81%. Note: This reaction does not proceed if pentane is used instead of diethylether ( $\text{Et}_2\text{O}$ ) as the solvent.  
15  
20

Preparation of  $(\text{C}_5(\text{CH}_3)_4-\text{Si}(\text{CH}_3)_2-\text{p}-\text{C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}_2(1-\text{Pr}_2\text{O})_4)$  (3): n-BuLi (1.15 mL, 2.5 M in hexanes) was syringed into a stirred  $-78^{\circ}\text{C}$  isopropyl ether (~40 mL) solution of 2 and then warmed to room temperature on its own. Stirring was continued overnight and left a white solid suspended in solution. The isopropyl ether was removed via cannula filtration to leave a white crystalline solid which was then washed 1x with pentane (20 mL) and pumped dry. Yield 2.54 g, 77%. Note: Removal of the Cp methine proton does not proceed to completion in either  $\text{Et}_2\text{O}$  or THF due to the formation of an oily layer at the bottom, possibly a calathrate. Longer reaction times (2.5 days) produces no difference in the recovered yield of 3. Use of greater than 1 equivalent of n-BuLi is also ineffective. Use of a smaller alkyl lithium  
25  
30

- 12 -

such as methyl lithium (MeLi) does not work either. A mixture of unidentified products is recovered in this case. The use of lithium dimethyl amide ( $\text{LiN}(\text{CH}_3)_2$ ) produces results similar to that when 1.1 equivalent of n-BuLi is used (i.e. - 50% conversion to 3).

Preparation of  $(\text{ZrCl}_4, (\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{i-Pr}_2\text{O})_4)$  (4): 0.708 g of 3 was suspended in i-Pr<sub>2</sub>O (~10 mL) and cooled to -78 C. 1.1 equiv. of  $\text{ZrCl}_4$  (144 mgs) was then added slowly via side arm addition funnel. Upon addition, a yellow oil formed but the reaction was allowed to warm to room temperature and stirred overnight. The solution was concentrated and when the stirring was stopped a yellow oil layer was deposited at the bottom of the flask. The excess (iPr)<sub>2</sub>O was cannulated off, then pumped dry. The product was then dissolved in ~30 mL  $\text{CH}_2\text{Cl}_2$  and left to let the salts settle. The supernatant was then filtered through medium porosity filter paper. The  $\text{CH}_2\text{Cl}_2$  was removed to leave a yellow crystalline solid. Successive recrystallization from  $\text{CH}_2\text{Cl}_2$  /pentane left a yellow oily solid which became crystalline after vacuum was applied. Yield .790 g, 52%.

Note: Mixing 3 and  $\text{ZrCl}_4$  in a 1:1 ratio together before adding cold i-Pr<sub>2</sub>O produces similar results. Likewise, vacuum transferring i-Pr<sub>2</sub>O onto 3 and  $\text{ZrCl}_4$  also gives 4. In all cases, the product needs to be washed with a little i-Pr<sub>2</sub>O to remove any 2 which is formed in the reaction. Use of only .95 equiv. of  $\text{ZrCl}_4$  in any reaction leaves traces of 3 which cannot be removed easily. If the reaction is done in  $\text{CH}_2\text{Cl}_2$  some decomposition of the ligand is observed.

Preparation of  $(\text{Zr}(\text{CH}_2\text{Ph})_3, (\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3 \cdot \text{Li}(\text{Et}_2\text{O})_4)$  (5): 0.200 g of 4 was suspended in ~10 mL of Et<sub>2</sub>O and cooled to -78°. BzMgCl (161  $\mu\text{L}$ , 3.2 eq) was syringed in and the reaction was allowed to warm to room temperature. A bright yellow solution formed immediately and

- 13 -

was left stirring for 8 hrs. Solvent was stripped and the product dissolved in  $\text{CH}_2\text{Cl}_2$  to separate the salts. The solution was cannula filtered and dried under vacuum to leave a bright yellow solid. Yield not established. Note: This reaction does not proceed well in  $i\text{-Pr}_2\text{O}$ .

Preparation of  $(\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3\text{Li}(i\text{-Pr}_2\text{O})_4)$  (6): .475 g of 4 was mixed with .045 g of  $\text{LiCp-SiMe}_3$  (base free). -10 mL of cold ( $-78^\circ\text{C}$ )  $\text{CH}_2\text{Cl}_2$  was cannulated onto the two solids and stirred at room temperature for 2 hrs. A yellow solution formed. Stirring was stopped, the salts were allowed to settle and the solution was collected via cannula filtration. Successive  $\text{CH}_2\text{Cl}_2$ /pentane recrystallizations left a yellow crystalline solid. Yield is quantitative by  $^1\text{HNMR}$ .

Preparation of  $(\text{Zr}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_4)\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3\text{Li}(i\text{-Pr}_2\text{O})_4)$  (7): .175 g of (6) was suspended in -10 mL of  $\text{Et}_2\text{O}$  and cooled to  $-78^\circ\text{C}$ . 2.5 equiv.  $\text{CH}_3\text{MrBr}$  was syringed in and the reaction kept cold for 1 hr. It was then warmed to room temperature and stirred for 5 hrs. The resulting solution was filtered and then solvent was removed under vacuum to leave a yellow solid.

In situ generation of  $[\text{Zr}(\text{CH}_3)(\text{THF})(\eta^5\text{-C}_5\text{H}_4\text{Si}(\text{CH}_3)_3)(\eta^5\text{-C}_5(\text{CH}_3)_4\text{-Si}(\text{CH}_3)_2\text{-p-C}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3)]$ ; 0.33 g of (7) was dissolved in  $\text{THF}_{d-8}$  and cooled to  $-10^\circ\text{C}$ . One equivalent of tris-pentafluorophenyl boron was then added via spatula to the sample and warmed to room temperature immediately. A  $^1\text{HNMR}$  spectrum was recorded within 10 minutes and exhibited resonances consistent with the formation of the compound. Spectroscopic data:  $^1\text{HNMR}$   $\delta$ -0.22 (s, 3H,  $\text{Zr-CH}_3$ );  $\delta$ 0.63 (br s, 6H,  $\text{Si}(\text{CH}_3)_2$ -);  $\delta$ 0.30 (2, 9H,  $-\text{Si}(\text{CH}_3)_3$ );  $\delta$ 1.79 (s, 3H,  $\text{Cp-CH}_3$ );  $\delta$ 1.88 (2, 3H,  $\text{Cp-CH}_3$ );  $\delta$ 1.99 (s, 3H,  $\text{Cp-CH}_3$ );  $\delta$ 1.99 (s, 3H,  $\text{Cp-CH}_3$ );  $\delta$ 5.72 (br s, 1H,  $\text{TMS-Cp}$ );  $\delta$ 5.95 (br s, 1H,  $\text{TMS-Cp}$ );  $\delta$ 6.40 (br

- 14 -

s, 1H, TMS-Cp);  $\delta$ 6.50 (br s, 1H, TMS-Cp).

#### CATALYST PREPARATION

All procedures were performed under a dry nitrogen atmosphere. All liquids/solvents were anhydrous.

5 Catalyst A, 15 mg (0.0097 mmol) of  $(Zr(Cl_2[(\eta^5-C_5H_4)(Si(CH_3)_3)](\eta^5-C_5(CH_3)_4)-Si(CH_3)_2-p-C_6F_4B(C_6F_3)] \cdot Li(O-i-Pr_2O)_4)$  were dissolved in 2.0 g of a MAO/toluene solution (13 weight percent aluminum, 9.63 mmol Al, Al/Zr=1000) at room temperature. The catalyst was used immediately after  
10 preparation.

Catalyst B, 4 mg (0.0099 mmol) of  $(\eta^5-C_5H_4-n-Bu)_2ZrCl_2$  were dissolved in 2.0 g of a MAO/toluene solution (13 wt.% aluminum, 9.63 mmol Al, Al/Zr = 1000) at room temperature.

#### POLYMERIZATION

15 Ethylene/1-hexene copolymers were prepared by these catalysts under identical polymerization procedures, described below:

A 1 gallon stainless steel autoclave at room temperature was charged with 1500 mL heptane and 150 mL 1-hexene. 1.0 mL  
20 of 14 weight percent tri-iso-butylaluminum in hexane were added. The reactor was closed, and the temperature was brought to 70°C. 50 mg of catalyst B was introduced with ethylene pressure. Ethylene was replenished on demand to keep reactor pressure constant at 135 psi. After 60 minutes,  
25 the reactor was vented and cooled to room temperature. 42.1 gm polymer were collected.

	Catalyst	A	B
	Activity		
	kg/gZr/hr	170	1870
30	I <sub>2</sub> (g/10 min.)	0.07	0.04
	MFR	17.3	18.1
	Density (g/cc)	0.916	0.917
	Mole % C <sub>6</sub>	2.1	1.0
	Melting Pt. (°C)	111.2	118.5



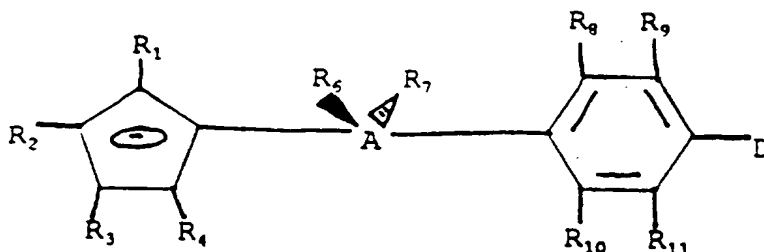
## CLAIMS:

1. A compound of the formula

(V) (E) (W) M-L

in which M is selected from the group consisting  
5 of zirconium, hafnium and titanium;

in which each of V, E, W is the same or different  
and each is alkyl of 1 to 6 carbon atoms, halide, or  
unsubstituted or substituted cyclopentadienyl provided that  
one, and only one, of V, E, and W, is unsubstituted or  
10 substituted cyclopentadienyl; and in which L is



wherein each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, is hydrogen, alkyl of 1  
to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which  
form bridged bicyclic or tricyclic moieties;

A is C, Si, Ge; and each of R<sub>6</sub> and R<sub>7</sub> is the same or  
15 different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to  
20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl  
of 3 to 20 carbon atoms;

each of R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, is the same or different, and  
is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

20 D is hydrogen, alkyl of 1 to 6 carbon atoms, sodium,  
lithium, halogen, BG<sub>3</sub> or AlG<sub>3</sub> in which B is boron (B) and Al  
is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl,  
phenyl or alkyl of 1 to 6 carbon atoms.

25 2. The compound of Claim 1, wherein D is BG<sub>3</sub>.

3. The compound of Claim 2, wherein G is pentafluorophenyl.

4. The compound of Claim 1, wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ , is methyl.

5. The compound of Claim 1, wherein A is Si.

6. The compound of Claim 5, wherein each of  $R_6$  and  $R_7$  is alkyl of 1 to 6 carbon atoms.

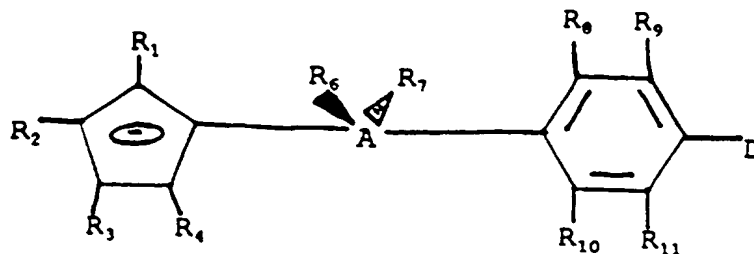
7. The compound of claim 6, wherein G is pentafluorophenyl.

8. A compound of the empirical formula  
(V) (E) (L) M<sup>+</sup>

in which M is selected from the group consisting of zirconium, hafnium and titanium;

5 in which each of V and E is the same or different and each is alkyl of 1 to 6 carbon atoms, halide, or unsubstituted or substituted cyclopentadienyl provided that one, and only one, of V, and E is unsubstituted or substituted cyclopentadienyl;

10 and in which L is



wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

- 17 -

A is C, Si, or Ge; and each of R<sub>6</sub> and R<sub>7</sub> is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

5 each of R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms; sodium; lithium; halogen; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; or BG<sub>3</sub> or  
10 AlG<sub>3</sub> in which B is boron (B) and Al is aluminum (Al),

G is selected from the group consisting of pentafluorophenyl, trifluoromethyl, phenyl, hydrogen and alkyl of 1 to 6 carbon atoms.

9. The compound of Claim 8, wherein A is Si.

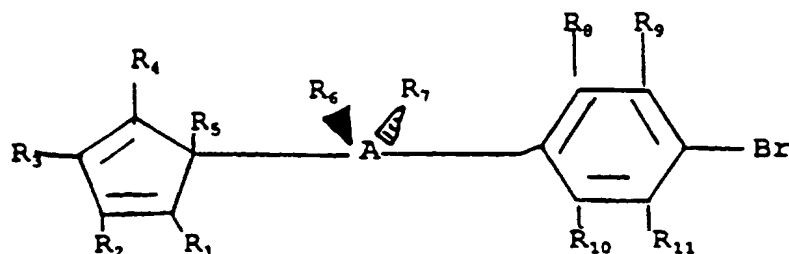
10. The compound of Claim 9, wherein each of R<sub>6</sub> and R<sub>7</sub> is alkyl of 1 to 6 carbon atoms.

11. The compound of claim 10, wherein G is pentafluorophenyl.

12. A process for olefin polymerization comprising contacting ethylene with a transition metal catalyst, under olefin polymerization conditions, in which the source of transition metal is the compound of Claim 1.

13. A process for olefin polymerization comprising contacting ethylene with a transition metal catalyst, under olefin polymerization conditions, in which the source of transition metal is the zwitterion of Claim 8.

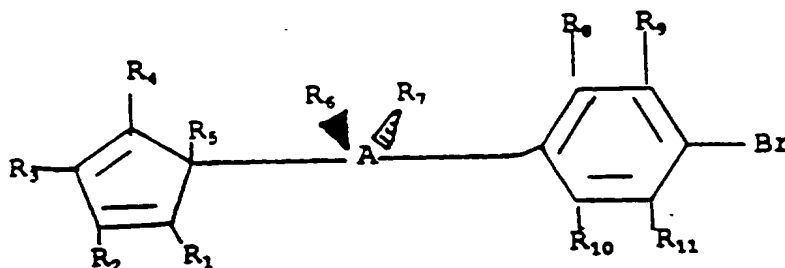
14. A process for forming the compound of Claim 1 comprising contacting a compound of the formula



with a reagent effective to abstract the R<sub>5</sub> group to form an intermediate and contacting the intermediate with a transition metal halide, in which the transition metal is selected from the group consisting of zirconium, hafnium and titanium, to form a trihalide transition metal salt of the intermediate.

15. The process of claim 14, which further comprises the step of contacting the trihalide transition metal salt with a compound which is a lithium salt of cyclopentadienyl compound which comprises an unsubstituted or substituted cyclopentadienyl ring which is mono, di-, tri, tetra or penta-substituted cyclopentadienyl, in which the substitution is monoalkyl, dialkyl, trialkyl, tetraalkyl or pentaalkyl-substituted cyclopentadienyl in which the alkyl is 1 to 6 carbon atoms.

16. A salt in which the anion is characterized by the formula



wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

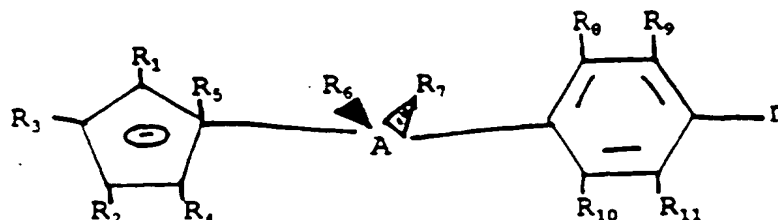
A is C, Si, Ge; and each of  $R_6$  and  $R_7$  is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

each of  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and halide is chlorine or bromine; and  $BG_3$  or  $AlG_3$  in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

17. A compound of the formula



- 20 -

wherein each of  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  is hydrogen, alkyl of 1 to 6 carbon atoms, alkylene of 2 to 10 carbon atoms which form bridged bicyclic or tricyclic moieties;

5  $R_5$  is hydrogen or  $GeZ_2$ , wherein Ge is germanium and Z is hydrogen or all alkyl of 1 to 6 carbon atoms;

A is C, Si, Ge; and each of  $R_6$  and  $R_7$  is the same or different and is alkyl of 1 to 20 carbon atoms, aryl of 6 to 20 carbon atoms, alkenyl of 2 to 20 carbon atoms or alkynyl of 3 to 20 carbon atoms;

10 each of  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ , is the same or different, and is fluorine, hydrogen, alkyl of 1 to 6 carbon atoms;

D is hydrogen, alkyl of 1 to 6 carbon atoms, alkali metal [sodium or lithium]; halogen [chloride or bromide]; alkyl halide in which the alkyl has 1 to 6 carbon atoms and  
15 halide is chlorine or bromine; and  $BG_3$  or  $AlG_3$ , in which B is boron (B) or Al is aluminum (Al), and

G is pentafluorophenyl, bis-trifluoromethylphenyl, phenyl or alkyl of 1 to 6 carbon atoms.

18. The compound of Claim 17, wherein D is Br.

20 19. The compound of Claim 17, wherein D is Li.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/11074

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07F 17/00, 7/00; B01J 31/00; C08F 4/44, 110/02

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/ 152, 157, 158; 526/ 127, 160, 352, 943; 556/ 7, 11, 12, 27, 28, 53

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
REGISTRY and CA databases

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DORMOND et al. Synthese D'un Ligand Cyclopentadienyle Optiquement Actif Applications En Chimie Organometallique. Tetrahedron Letters. 1983, Vol. 24, No. 30, pages 3087-3090, especially compound 3 on page 3088.	1-19
A	SCHMID et al. $\eta^5$ -Pentabenzylcyclopentadienyl derivatives of titanium (IV), (III), and (II). The crystal structures of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Bz}_5)\text{TiCl}_2$ (Bz = benzyl), $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Bz}_5)\text{Ti}[\eta^2\text{-(CSiMe}_3)_2]$ . Journal of Organometallic Chemistry. 1994, Vol. 482, pages 231-241, especially 237.	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* B* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* A*	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

26 AUGUST 1997

Date of mailing of the international search report

10 OCT 1997

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Form PCT/ISA/210 (second sheet)(July 1992)\*

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/11074

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BULLS et al. Relative bond dissociation energies for early transition metal alkyl, aryl, alkynyl and hydride compounds. Equilibration of metallated cyclopentadienyl derivatives of peralkylated hafnocene and scandocene with hydrocarbons and dihydrogen. Polyhedron. 1988, Vol. 7, No 16/17, pages 1409-1428, especially page 1413.	1-19
A	HOWELER et al. A Valence Force Field for Zirconocene Dichlorides. Organometallics. June 1994, Vol. 13, No. 6, pages 2380-2390, especially compounds 3 and 9 on page 2384.	1-19

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/11074

## A. CLASSIFICATION OF SUBJECT MATTER: US CL :

502/ 152, 157, 158; 526/ 127, 160, 352, 943; 556/ 7, 11, 12, 27, 28, 53